

## Mineralogical and geochemical profiling of Arsenic-contaminated aquifers in central Bangladesh

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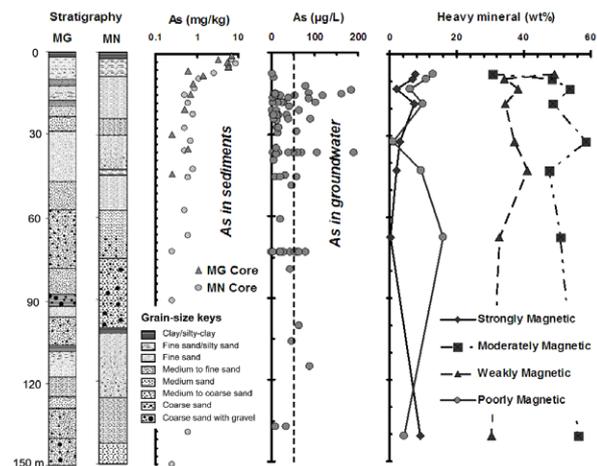
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Groundwater of shallow (<100 m below ground level) alluvial aquifers in Bangladesh and West Bengal, India is contaminated with elevated (>50  $\mu\text{g/L}$ ) aqueous arsenic (As) concentrations. Microbial reduction of As-bearing Fe-oxhydroxides (FeOOH) is the widely accepted mechanism for elevated As in groundwater although geological control on its spatial distribution, however, remains uncertain. We analyzed 85 groundwater and 32 cored sediment samples (2–150 m bgl) collected at Manikganj district in central Bangladesh. Stratigraphy shows typical fining upward sequences composed of sub-arkosic to arkosic sands. Sediments at shallow depth contain more biotite, magnetite, amphibole, apatite, and authigenic FeOOH (goethite) than sediments at greater depths (Figure 1). Microprobe analysis of goethite reveals high amount (~340 mg/kg) of solid-phase As in sediments. Abundant FeOOH and Fe-bearing minerals such as magnetite, apatite, and biotite are potential carriers of As in sediments. Geologic heterogeneity and variations in the magnitude of aquifer flushing strongly influence As distributions in alluvial aquifers in the Bengal Basin.



**Figure 1:** Stratigraphy, As contents in sediments, groundwater, and heavy mineral contents in sediments.

## Stable isotopic fingerprints of greenhouse gasses before the rise of oxygen

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Chemical compositions of early Earth's atmosphere have been largely unknown. In the Archean, abundances of greenhouse gasses are believed to have been much higher than today's for maintaining warm climate under less bright young Sun [1]. Not only higher  $\text{CO}_2$  levels but also additional greenhouse gasses may have been required. Biological  $\text{CH}_4$  was likely accumulated in the anoxic early atmosphere, though contribution of  $\text{CH}_4$  to the radiative forcing is still debated [2, 3]. An alternative candidate is carbonyl sulfide (OCS), which is more effective greenhouse gas than  $\text{CO}_2$  and  $\text{CH}_4$ . Our laboratory experiments and numerical simulations suggest that elevated levels of OCS (>1 ppm) can be maintained if the atmosphere is reducing and rich in CO (>1%) [4]. Mass independent fractionation of sulfur isotopes (S-MIF) can be useful to test the scenario [5]. Although mechanisms of the S-MIF has not been fully understood, S-MIF is produced by photolysis of  $\text{SO}_2$  in an anoxic atmosphere. We have determined UV absorption spectra of  $^{32}\text{SO}_2$ ,  $^{33}\text{SO}_2$ , and  $^{34}\text{SO}_2$  and described sulfur isotope fractionation factors as a function of wavelength [6]. Based on the estimated wavelength-dependence of the S-MIF, we suggested that UV-shielding by OCS results in distinctive UV actinic spectra and can explain negative  $\Delta^{33}\text{S}$  recorded in all the Archean sulfate deposits [4]. UV-shielding by  $\text{SO}_2$  (self-shielding) might have alternative effect on S-MIF [7], though such high  $\text{SO}_2$  level (>1ppm) is difficult to maintain unless volcanic  $\text{SO}_2$  flux is extraordinary high. Oxygenation of the atmosphere should decrease the atmospheric OCS levels and quantitative conversion of all atmospheric sulfur species into  $\text{H}_2\text{SO}_4$ , both of which result in cooling of surface temperature. Thus, the atmospheric sulfur cycling including OCS chemistry would have been more important for Archean climate than previously thought.

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